

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Methods for Dyeing Hair and like Keratinous Materials

We, SOCIETE MONSAVON-L'OREAL, a French body corporate, of 14, rue Royale, Paris 8ème, (Seine), France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods for dyeing hair, particularly human hair, and like keratinous materials.

In our Application No. 22892/56 (Serial No. 797,174) we have described a process for dyeing human hair and other keratinous fibres which consists essentially in (a) preparing an aqueous solution adjusted to an alkaline pH, containing 5:6-dihydroxy-indole and ammonia, an amine, or an ammonium salt (b) applying this solution to the hair or similar material to be dyed and rinsing the latter after a period of contact varying in accordance with the desired shade. In this way, relatively light shades ranging from light ash-blond to dark ash-blond are obtained for a standard period of contact of the order from 20 to 30 minutes at room temperature, which period may be reduced by slight heating, for example, in the case of hair-dyeing, by means of a dry heat hood or a steam hood. It is furthermore possible, in accordance with the method of the aforesaid application, to obtain a more rapid development of the shade by adding to the dyeing solution, at the time of application, an oxidising agent, such as sodium bromate, a persalt such as sodium perborate or ammonium persulphate, or simply hydrogen peroxide. There is to be noted that where an oxidising agent is used it is necessary to make a well-balanced choice of the quantity added, a minimum quantity being necessary for a sufficiently rapid formation of the coloured pigments while an excess of this agent has the effect of more or less destroying said coloured pigments intermediately formed and thus of reducing the depth of the final shade.

As indicated in said application, it is pos-

sible to obtain dark shades closely comparable to the natural shades of the hair by operating in two steps, i.e. by first treating the hair with an alkaline solution of 5:6-dihydroxy-indole at room temperature for 15 to 30 minutes and then, after rinsing with water, applying to the hair a solution of an oxidation catalyst.

It is an object of the present invention to provide a process for the dyeing of human hair and like keratinous fibres by means of 5:6-dihydroxy-indole while still operating in two steps, wherein the 5:6-dihydroxy-indole solution applied in the first step, instead of being alkaline is either acid or neutral.

According to the present invention a process for dyeing live hair and like keratinous materials consists essentially in impregnating the hair or like keratinous material at room temperature with an aqueous solution of 5:6-dihydroxy-indole having a pH-value of at most 7, allowing the impregnation to proceed for about 5 to 60 minutes, blotting off the excess solution, and developing the shade *in situ* by applying an aqueous solution capable of inducing oxidation of 5:6-dihydroxy-indole.

The pH-value of the aqueous 5:6-dihydroxy-indole solution to be applied in a first step for carrying out the invention may be obtained in various ways. For example, there may be employed an aqueous solution only containing the 5:6-dihydroxy-indole, with the exclusion of any other reactant, the pH-value of such a solution being of course slightly acid. It is also possible to acidify this aqueous solution more or less strongly, for example by means of an inorganic acid, an organic acid, e.g. formic, acetic or monochloroacetic acid, or any compound containing at least one acid hydrogen atom.

The concentration of 5:6-dihydroxy-indole in the solution as applied to the hair or other keratinous material may vary within fairly wide limits. Generally it will be between 0.1% and 10% and preferably between 1% and 2% by weight of the solution. The term

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- "aqueous solution" as employed here means any solution the principal solvent of which is water. It is of course possible, without departing from the scope of the invention, to use in the preparation of such a solution water alone or in admixture with the water-miscible solvents, notably mixtures of water and ethyl alcohol or isopropyl alcohol or water and glycols or glycol ethers.
- The aqueous solution of 5:6-dihydroxy-indole to be applied first may be prepared at the time of use. However, 5:6-dihydroxy-indole, like many other organic compounds, is relatively much more stable in acid or neutral medium than in alkaline medium and it is possible to have it prepared in advance in the form of any aqueous solution and, whenever desired, further to improve the stability of such a solution by adding thereto a small amount of a reducing agent, such as, for example, an alkali metal sulphite, bisulphite of hydrosulphite, this addition preferably being made first, i.e. before the 5:6-dihydroxy-indole is added. The stability of aqueous solutions of 5:6-dihydroxy-indole may also be enhanced by adding thereto a small quantity preferably 0.2% to 0.5% by weight, of a sequestering agent, i.e. a compound capable of forming complexes with ions of alkaline-earth metals or of heavy metals, often existing as trace impurities. The sequestering agent may be, for example, ethylenediamine-tetracetic acid or one of its salts, such as that known under the Registered Trade Mark "Trilon" B.
- When the aqueous 5:6-dihydroxy-indole solution has been in contact with the hair or other material for a period of 5 to 60 minutes the excess solution is blotted off, for example by pressing the hair in a towel.
- The shade is then developed *in situ* by applying to the hair or other keratinous material an aqueous solution capable of inducing oxidation of the 5:6-dihydroxy-indole.
- The choice of this oxidation inducing solution, as also the length of time during which it should be maintained in contact with the hair or the other keratinous material to be dyed, depends to some extent upon the final shade it is desired to obtain. It is also possible to predetermine the final shade by adjusting the pH of the developing solution to a pre-selected value, e.g. by including acid or alkaline materials therein.
- In one method of carrying out the process of the invention there is used as oxidising agent the oxygen of the ambient air, if desired ozonised. In such an embodiment the development of the shade, which amounts to the rapid fixing of the atmospheric oxygen by the hair or similar material impregnated with 5:6-dihydroxy-indole, is effected by applying in a second step as a developing medium an aqueous solution containing an alkaline substance consisting preferably of ammonia, a basic ammonium salt such as ammonium carbonate or triammonium phosphate, or an organic amine. It is generally advantageous also to incorporate in this solution an oxidation catalyst which accelerates the process of fixing the oxygen of the ambient air, for example small quantities of a cobalt or manganese, salt, such as the sulphate or the lactate. The aqueous solution containing the alkaline substance and, if desired, the oxidation catalyst is left in contact with the hair or similar material for 10 to 60 minutes as necessary for the penetration of the reactants. The hair is then rinsed clear with water and dried. The development of the shade, which is initiated by the alkalisation, may proceed for some time, this process then constituting a progressive dyeing process.
- In a second method of carrying out the invention, there is applied in a second step, for the development of the shade, an aqueous solution of an oxidizing agent, such as, for example, hydrogen peroxide, or an alkali metal or ammonium iodate, periodate, or persulphate or an alkali metal salt of an N-chlorinated derivative of a sulphonamide. This solution is allowed to act for a period of time sufficient for the development of the shade, generally from 5 to 20 minutes, and the hair is then rinsed, shampooed, rinsed again and dried. The pH of this aqueous oxidising solution, applied in the second place, may be adjusted to any desired value, either acid, neutral or alkaline, by the addition of any appropriate reactant, for example an inorganic or organic acid, a salt having an acid reaction, a buffer, a salt having a basic reaction or a base such as ammonia or an organic amine. The choice of the most suitable value depends mainly, but not solely, upon the nature of the oxidising agent employed. If the latter is hydrogen peroxide, an alkali metal or ammonium iodate or periodate or an alkali metal salt of an N-chlorinated derivative of a sulphonamide, it is generally preferably to operate in a basic medium, whereas the operation is preferably carried out in an acid medium if the oxidising agent is an alkali metal or ammonium persulphate. However, if the oxidising agent employed is an iodate or a periodate, it is preferable not to operate at a pH-value lower than 3 and to avoid the use of a strong inorganic acid for adjusting the pH to the desired value.
- Whatever the pH chosen for the development of the shade, the concentration of the oxidising agent in the aqueous solution may be chosen between fairly wide limits, depending upon the desired shade and upon the own solubility of the specific oxidising agent which is to be used. Generally speaking, the quantity of oxidising agent to be employed corresponds to 0.5 to 10 g. per 100 cc. of solution, the volume of oxidising solution to be

employed being substantially the same as the quantity of dihydroxyindole solution.

When the oxidising solution employed in the second step is acid or neutral, i.e. free from ammonia and organic amines, it is probable that the pigment formed results from the formation of the quinone corresponding to 5, 6-dihydroxyindole. However analytical data has shown that if the oxidising solutions are rendered alkaline by means of ammonia or an amine, the molecule of the pigment obtained contains nitrogen issuing from the ammonia or the amine employed. The same holds true when the oxidation is effected through the intermediary of ambient air and in the presence of ammonia or an amine, according to the first embodiment of the invention.

According to an accessory feature of the invention and whatever the specific embodiment to be dealt with, there can be advantageously added to the developing solution a quantity of a neutral, strongly ionised inexpensive electrolyte such as, for example, sodium chloride or sodium sulphate.

The dyeing process according to the invention may be carried out, not only by means of aqueous solutions as referred to above, but also by means of aqueous creams, pastes or jellies, the adjustment to the required consistency being effected by any method usual in hair dyeing.

The use of 5,6-dihydroxy-indole, under the above-defined conditions, constituting the object of the present invention may be combined with that of di- or tri-hydric phenols capable of dyeing hair and other keratinous fibres at room temperature.

The following examples will serve to illustrate the invention:—

Example I illustrates the case where the development is effected in a basic medium and by oxidation in the ambient air, while the other examples illustrate cases where the development is effected by means of an oxidising solution.

#### EXAMPLE I.

An impregnating solution having the following composition is prepared:—

5,6-dihydroxy-indole	-	-	-	1 g.
Acetic acid	-	-	-	5 cc.
Water to make	-	-	-	100 cc.

Naturally white or nearly white live hair is impregnated with this solution. After contact for 20 minutes, the excess solution is blotted off, for example by means of a towel, and an aqueous solution having the following composition is then applied.

Sodium chloride	-	-	-	4 g.
Water	-	-	-	100 cc.
20% ammonia	-	-	-	17 cc.

After contact for 20 minutes, the hair is rinsed clear with water and dried. The hair is dyed a dark grey which gradually changes to black. (This constitutes a progressive dyeing).

#### EXAMPLE II

An impregnating solution as set forth in Example I is applied to naturally white live hair.

This solution is left in contact with the hair for 20 minutes, then blotted off, and the following solution is then applied:—

Sodium chloride	-	-	-	4 g.
Hydrogen peroxide (20 vol.)	-	-	-	
(6% of $H_2O_2$ )	-	-	-	2.5 cc.
Water to make	-	-	-	100 cc.

This solution is left in contact with the hair for 1 hour, and the hair is then rinsed, shampooed, rinsed again and dried. A light grey shade is obtained, which remains substantially unchanged in the following weeks.

#### EXAMPLE III.

Almost white live hair is impregnated with an impregnating solution as set forth in Example I. After contact for 20 minutes, the excess solution is blotted off and a second solution having the following composition is then applied:—

Sodium chloride	-	-	-	4 g.
Water	-	-	-	100 cc.
20% ammonia	-	-	-	17 cc.
Hydrogen peroxide (20 vol.)	-	-	-	
(6% of $H_2O_2$ )	-	-	-	0.3 cc.

This second solution is left in contact with the hair for 30 minutes, and the hair is then rinsed shampooed, rinsed again and dried. The hair is dyed jet-black.

#### EXAMPLE IV.

Almost white live hair is impregnated with an impregnating solution as set forth in Example I.

After contact for 20 minutes, the excess solution is blotted off and the following solution is then applied:—

Sodium chloride	-	-	-	4 g.
Monomethylamine (in 33% aqueous solution)	-	-	-	10 cc.
Hydrogen peroxide (20 vol.)	-	-	-	
(6% of $H_2O_2$ )	-	-	-	2.5 cc.
Water to make	-	-	-	100 cc.

This solution is left in contact with the hair for 20 minutes, and the hair is then rinsed, shampooed, rinsed again and dried. The hair is dyed medium ash-blond.

#### EXAMPLE V.

Nearly white live hair is impregnated with an impregnating solution as defined in Example I. After a period of contact of 20 minutes, the excess solution is blotted off and an aqueous solution having the following composition is applied:—

Sodium chloride	-	-	-	2.8 g.
20% ammonia	-	-	-	6 cc.
Hydrogen peroxide (20 vol.)	-	-	-	
(6% of $H_2O_2$ )	-	-	-	23 cc.
Water to make	-	-	-	100 cc.

After contact for 20 minutes, the hair is

rinsed, shampooed, rinsed again and dried. A medium brown shade is obtained.

#### EXAMPLE VI.

5 Naturally white or nearly white hair is impregnated with an impregnating solution as defined in Example I.

The solution is left in contact for 20 minutes, whereafter the excess solution is blotted off and an aqueous solution having

10 the following composition is applied:—  
Sodium chloride - - - 3.2 g.  
20% ammonia - - - 2 cc.  
Hydrogen peroxide (20 vol.)  
(6% of  $H_2O_2$ ) - - - 16 cc.

15 Water to make - - - 100 cc.

This solution is left in contact with the hair for 20 minutes, the hair is then rinsed, shampooed, rinsed again and dried. A light brown shade is obtained.

#### EXAMPLE VII.

20 Naturally white live hair is treated with an impregnating solution as defined in Example I.

This solution is left in contact with the hair for 30 minutes, whereafter the excess solution is blotted off and an aqueous solution having the following composition is applied to the hair.

25 Sodium chloride - - - 5 g.  
Triethanolamine - - - 26 cc.  
30 Hydrogen peroxide (20 vol.)  
(6% of  $H_2O_2$ ) - - - 10 cc.  
Water - - - 75 cc.

After contact for 30 minutes, rinsing, shampooing, rinsing again and drying, the hair is

35 dyed grey.

#### EXAMPLE VIII.

Almost white live hair is impregnated with an impregnating solution as defined in Example I, which is left in contact therewith

40 for 20 minutes. After blotting off the excess solution, the following solution is applied:—

Sodium chloride - - - 4.2 g.  
Chloramine T (sodium N-chloro-p-toluene sulphon-  
45 amide) - - - 1.2 g.  
20% ammonia - - - 14 cc.  
Water to make - - - 100 cc.

After contact for 20 minutes, the hair is rinsed, shampooed, rinsed again and dried.

50 The hair is dyed a fine deep black.

#### EXAMPLE IX.

Naturally white live hair is impregnated with the following impregnating solution:—

55 5,6-dihydroxy-indole - - - 1 g.  
Acetic acid - - - 0.5 cc.  
Water to make - - - 100 cc.

The pH-value of this solution is 3.3. This solution is left in contact with the hair for 15 minutes. The excess solution is then blotted off and an aqueous 4% by weight of sodium iodate solution is then applied to the hair.

60 After 15 minutes, the hair is rinsed, sham-

pooed, rinsed again and dried. A dark grey shade is obtained.

#### EXAMPLE X.

A solution having the following composition is prepared:—

5,6-dihydroxy-indole - - - 1 g.  
Water - - - 100 cc.

The pH-value of such a solution is 6.2.

This solution is applied to naturally white live hair and left in contact therewith for 15 minutes. After blotting off the excess solution, an aqueous 4% by weight sodium iodate solution is applied to the hair. After this solution has been allowed to act for 15 minutes, the hair is rinsed, shampooed, rinsed again and dried. The hair is dyed a dark grey, which is not, however, as dark as the shade obtained in Example IX.

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#### EXAMPLE XI.

Naturally white live hair is treated with an impregnating solution as defined in Example IX.

After contact for 15 minutes, the excess solution is blotted off and an aqueous 4% by weight sodium periodate solution is then applied to the hair. After contact for 15 minutes, rinsing, shampooing, rinsing again and drying, the hair is dyed in a grey shade which is a little lighter than that obtained in Example X.

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#### EXAMPLE XII.

A solution having the following composition is prepared:—

5,6-dihydroxy-indole - - - 1 g.  
Water - - - 100 cc.

This solution is applied to naturally white live hair and, after 15 minutes, the excess liquid is blotted off and an aqueous 4% by weight sodium periodate solution is then applied to the hair. After contact for 15 minutes, the hair is rinsed, shampooed, rinsed again and dried. The hair is dyed a light grey.

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#### EXAMPLE XIII.

Hair is impregnated with an impregnating solution as defined in Example IX.

This solution is left in contact with the hair for 15 minutes, whereafter the excess liquid is blotted off and an equal volume of an aqueous 5% by weight sodium persulphate solution is applied thereto. After 15 minutes, the hair is rinsed, shampooed, rinsed again and dried. A medium grey is obtained.

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#### EXAMPLE XIV.

An aqueous solution containing 1% by weight of 5,6-dihydroxy-indole is applied to naturally white live hair. This solution is left in contact with the hair for 15 minutes. The excess solution is then blotted off and an aqueous 5% by weight sodium persulphate solution is applied. After 15 minutes, the hair is rinsed, shampooed, rinsed again and dried. The shade obtained is medium grey.

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## EXAMPLE XV.

Naturally white live hair is impregnated with an impregnating solution as defined in Example I.

- 5 When this solution has been allowed to act for 20 minutes, the excess solution is blotted off and a solution having the following composition is applied:—

20% ammonia	- - - -	15 cc.
Sodium iodate	- - - -	0.5 g.
Water to make	- - - -	100 cc.

- 10 After contact for 20 minutes, the hair is rinsed, shampooed, rinsed again and dried. There is obtained a very dark grey shade having a violet tinge, gradually changing to black.

## EXAMPLE XVI.

- Almost white live hair is impregnated with an impregnating solution as defined in Example I which is left in contact therewith for 20 minutes. The excess solution is then blotted off and a solution having the following composition is applied thereto:—

Sodium periodate	- - - -	0.5 g.
20% ammonia	- - - -	15 cc.
Water to make	- - - -	100 cc.

- 25 This solution is allowed to act for 20 minutes and the hair is then rinsed, shampooed, rinsed again, and dried. There is directly obtained a fine black shade, which is substantially permanent.

## EXAMPLE XVII.

- Live, almost white hair is impregnated with an impregnating solution as defined in Example I.

- 35 After contact for 20 minutes, the excess liquid is blotted off and a solution having the following composition is applied to the hair:—

Ammonium persulphate	- - - -	0.5 g.
20% ammonia	- - - -	15 cc.
Water to make	- - - -	100 cc.

- 40 This solution is left in contact with the hair for 20 minutes. After rinsing, shampooing rinsing again and drying, the hair is dyed a fine deep black.

## EXAMPLE XVIII.

- A solution having the following composition is employed to impregnate almost white live hair:—

5,6-dihydroxy-indole	- - - -	1 g.
Monochloroacetic acid	- - - -	1 g.
Water to make	- - - -	100 cc.

- 50 After contact for 20 minutes with the hair, the excess liquid is blotted off and a solution having the following composition is applied:—

Ammonium persulphate	- - - -	6 g.
Sodium chloride	- - - -	4 g.
Monochloroacetic acid	- - - -	3 g.
Water to make	- - - -	100 cc.

- 60 This solution is left in contact with the air for 20 minutes, whereafter the hair is rinsed, shampooed, rinsed again and dried. The hair is dyed a medium grey.

It is to be understood that the invention includes dead hair or similar keratinous material dyed by employing the dying process according to the application e.g., hair, bristles, felt, fur and like keratinous products.

## WHAT WE CLAIM IS:—

1. A process for dyeing hair and like keratinous materials, including live hair, which consists essentially in impregnating the hair or like keratinous material at room temperature with an aqueous solution of 5,6-dihydroxy-indole having a pH-value of at most 7, allowing the impregnation to proceed for 5 to 60 minutes, then blotting off the excess solution and applying to the hair or like keratinous material an aqueous solution capable of inducing oxidation of the 5,6-dihydroxy-indole.

2. A process according to Claim 1 wherein said impregnating solution contains acetic acid or monochloroacetic acid.

3. A process according to Claim 1 or 2 wherein the concentration of the 5,6-dihydroxy-indole in the impregnating solution is 0.1 to 10% by weight.

4. A process according to Claim 3 wherein said concentration is 1 to 2% by weight.

5. A process according to any of Claims 1 to 4 wherein the aqueous solution capable of inducing oxidation is one which induces aerial oxidation.

6. A process according to Claim 5 wherein said solution contains ammonia, a basic ammonium salt or an organic amine.

7. A process according to Claim 5 or 6 wherein said solution also contains an oxidation catalyst.

8. A process according to any of Claims 1 to 4 wherein the solution applied to induce oxidation is one containing an oxidising agent.

9. A process according to Claim 8 wherein the oxidising agent is hydrogen peroxide, an alkali metal or ammonium iodate, periodate or persulphate or an alkali metal salt of an N-chlorinated derivative of a sulphonamide.

10. A process according to Claim 8 wherein the solution containing an oxidising agent is one containing hydrogen peroxide, an alkali metal or ammonium iodate or periodate or an alkali metal salt of an N-chlorinated derivative of a sulphonamide and is made alkaline.

11. A process according to Claim 8 wherein the solution containing an oxidising agent is one containing an alkali metal or ammonium persulphate and is made acid.

12. A process according to Claim 1 when carried out substantially as set forth in any one of the foregoing specific Examples I to XVIII.

13. Dead hair or like keratinous materials dyed by way of the processes hereinbefore disclosed and claimed.

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